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Internal curing agent in concrete and mortars

Application of Superabsorbent polymers as novel admixture for cementitious materials

Superabsorbent polymers (SAP) are novel materials to be used as internal curing agent in concrete and mortars. Their high capacity to absorb and release water can help to control cement hydration processes and hence to avoid cracking susceptibility in cementitious materials. The effect is usually evidenced by the reduction of autogenous shrinkage which is associated with self-desiccation process. This paper aims to present an overview of SAP application in cementitious composites and to illustrate their efficiency by comparing experimental results of mortars with and without SAPs. The paper argues that not only autogenous shrinkage may be reduced but depending upon the type of SAP mechanical characteristics may also be improved.

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Continuous improvement of specific properties and characteristics of traditional construction materials has recently led to the development of many new advanced composites. Durability and sustainability of these materials are more and more often the focus of investigations, especially in cement-based materials.

Despite their worldwide popularity, mortars and concrete may suffer from various deteriorative processes, leading to shortened service life and intrusive/expensive repairs. One of the causes of durability and performance losses is related to cracking susceptibility caused by autogenous shrinkage. This shrinkage can be defined as a macroscopic volume reduction of cementitious materials when cement hydrates after initial setting. It does not include volume change due to loss or ingress of substances, temperature variation, and application of an external force and restraint [1,2]. Autogenous shrinkage develops internally in the whole volume of concrete and may be associated with self-desiccation process. Even within the first few days after casting, autogenous shrinkage may lead to high restraint stresses and, thus, to crack formation in concrete, resulting in compromised mechanical properties and durability. This effect may still be aggravated in case of high-strength concrete that typically contains high cement content and low water-to-cement ratio. The only practical solution for prevention of the negative effects of shrinkage is to ensure a proper curing process [3].

Effective curing may be achieved by either external or internal methods. The first one is 'low-tech', physical method, which has no effect on the price of a given concrete mix. However, the necessary increase in labour demand, besides some practical constraints, often leads to a higher overall cost. Consistency of the finished product can be variable, as it is dependent on effective control in situ. The second method is based on application of internal curing agents. It is a promising way of mitigating human intervention on site, and in so doing leads to higher uniformity/consistency of the final product [4]. In this context, superabsorbent polymers (SAP) may have a potential application as an internal curing agent in cementitious materials [5].

SAP may be considered as a new admixture for cementitious materials, whose fine particles may serve as small water reservoirs evenly distributed across the concrete volume. Their high capacity to absorb water from fresh mix and to release it in either fresh or hardened state can lead to enhancement of some properties of concrete, for instance, autogenous shrinkage can be reduced. In cases of adequate internal curing, mechanical properties may also be improved as the pores formed by SAP can be filled (at least partially) by hydration products at later ages [6,7,8].

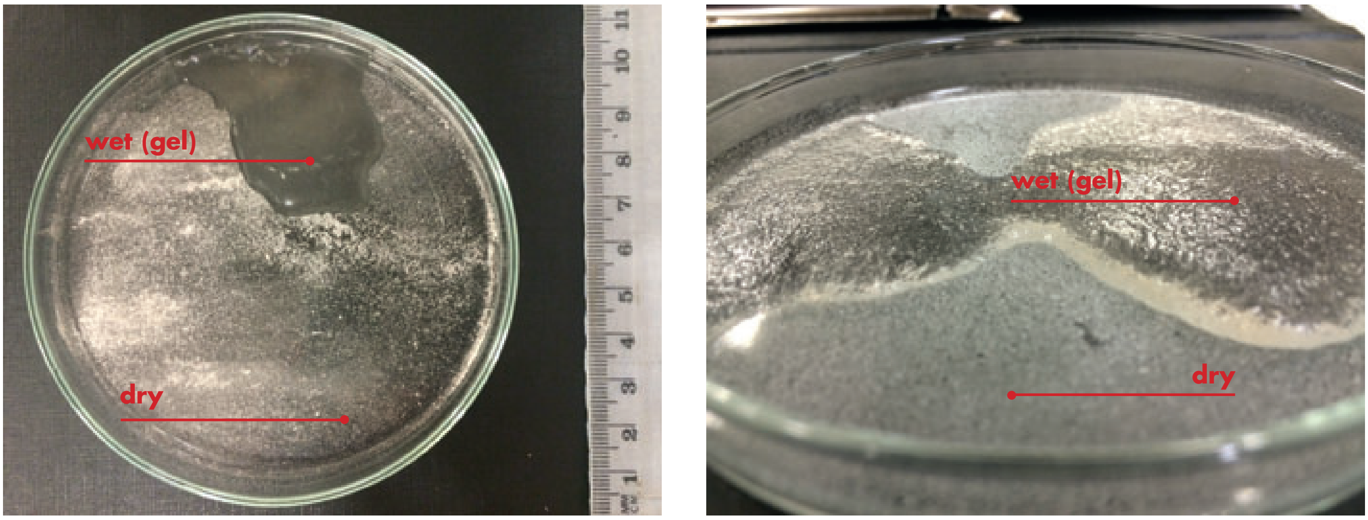

Fig. 1: Swelling process and gel formation of SAP

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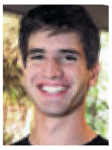

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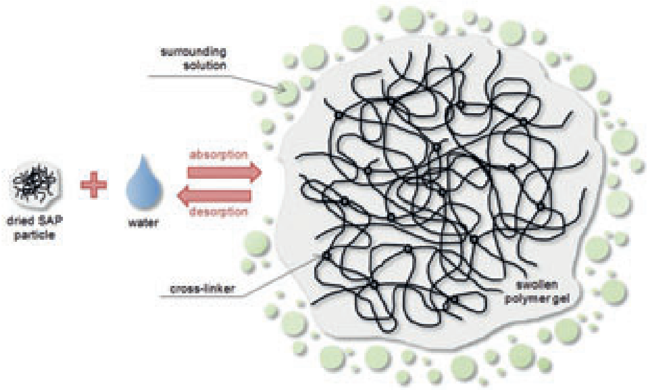

Fig. 2: Schematic representation of SAPs network in collapsed and swollen state

The recent studies undertaken by the RILEM Technical Committee 225-SAP "Application of Superabsorbent Polymers in Concrete Construction" focused on the possibilities and limitations of using SAP as a potential solution to various problems encountered by construction practitioners are very consistent and promising [5,9]. In order to further support this approach, this paper aims to illustrate SAP efficiency in cementitious matrices by presenting new experimental results in the context of the current state-of-the-art.

Superabsorbent polymers (SAP)

In principle superabsorbent polymers (SAP) are cross-linked networks of hydrophilic polymers with the ability to absorb and retain large volumes of water. In contact with water or aqueous solutions SAP hydrate and form a swollen polymer gel. These polymers are able to absorb even up to 1500 g of water per gram of SAP [5]. Figure 1 shows the swelling process of SAP and the formation of gel when water is added into the polymer.

SAPs are usually made from partially neutralised, lightly cross-linked acrylic acid and acrylamide or their modifications. This partial neutralization is often achieved by hydroxides of alkali metals, usually sodium. When their three-dimensional networks with chemical cross-links come into touch with fluid, water molecules diffuse into the void space inside the polymer network and hydrate the chains. The process of SAP hydration is reversible and the removal of water results in collapsing of the polymer [10] as shown on Figure 2.

The swelling capacity and strength of the network are directly determined by the degree of cross-linking, the chemical structures of

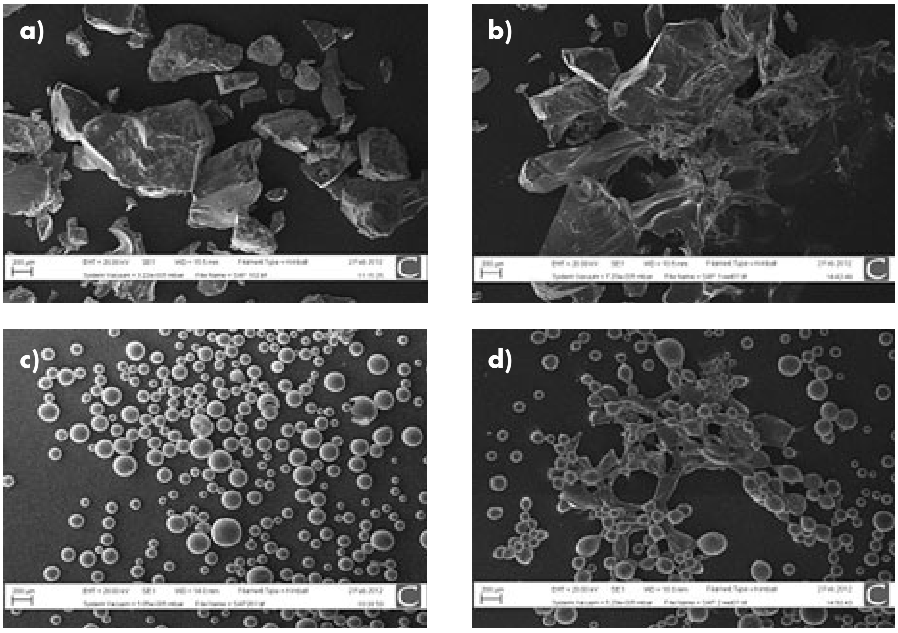

Fig. 3: The SEM micrographs of SAPs with different shapes in dry and wet conditions: (a) dry irregular particles; (b) wet irregular particles; (c) dry spherical particles; and (d) wet spherical particles [7]

monomers forming SAP network, and any external stimuli such as pH and ionic concentration in the surrounding [10].

SAPs with very high anionic functional group densities may take up liquids quickly and release it back into cement pore solution to a large extent over the first hours. In contrast, SAPs with lower anion density may store the absorbed liquid for longer and provide very moderate release of pore solution [11].

The concentration of cement pore solution, determined by the presence of Ca^{2+}, may also influence absorption and desorption behaviour of SAP [11]. Studies of swelling and absorption capacities [12] show different SAP behaviours when added to different solutions. While dry particles of SAP with diameters 158 µm achieved values of 955 µm in demineralized water, the same particles in synthetic cement-based pore fluid reached only 417 µm of diameter. These values correspond to absorption capacities of 144.4 ml/g in demineralized water and 11.6 ml/g in synthetic pore fluid.

The kinetics of liquid uptake into and release from SAP are very dependent on the ionic composition and concentration in a liquid, in particular KOH, Na_2SO_4 and Ca^{2+} in alkaline solution [11].

Besides that, the particles size may also influence the absorption kinetics and capacity. For instance, the lower a particle size, the faster absorption process. However, the absorption capacity is lower for decreasing particle diameters since less water is able to get into the cross-linked structure [13]. Moreover, gel blocking is a special property of very fine SAPs with particles size of less than 100 µm. If the SAPs are brought into contact water, little absorption takes place at the surface and the slightly swollen particles stick together. This results in lumps containing high amounts of not swollen SAP which do not disaggregate anymore. So, if fine SAPs are supposed to swell as individual particles, it is much more effective to distribute and disperse them before swelling [5].

SAP's shape and size are defined by their production technology [5]. The gel polymerisation technique demands a crushing process in the last production step, resulting in SAPs with irregular particle shapes. In this process, the dry particles are ground to the desired particle size. On the other hand, the inverse suspension polymerization generates spherical particles (single or raspberry like agglomerates); production of larger volumes of such SAPs is limited due to their higher cost. Figure 3 shows SAPs with irregular and spherical shapes in dry and wet conditions.

SAPs have a number of key parameters that can influence and control their efficiency. Characteristics defined by the production, as shapes, sizes and chemical structure compositions, affect their behaviour and performance in terms of absorption and desorption capacity/kinetics in demineralised water. Such effects can be even more complex when SAPs are applied in cementitious materials, when external conditions are substantially altered.

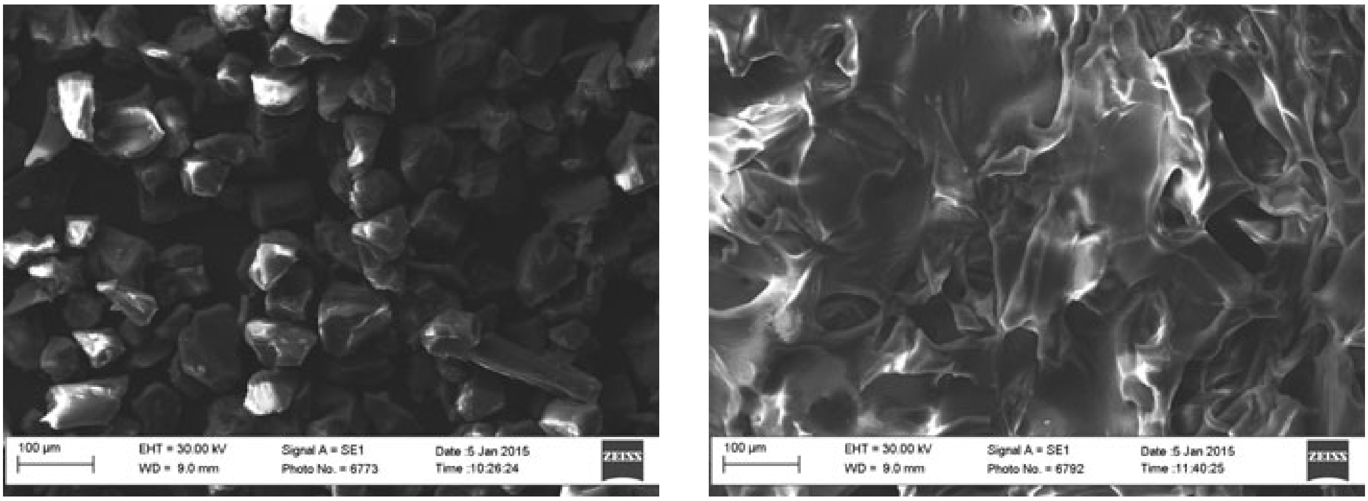

Fig. 4: The SEM micrographs of SAP X in dry and wet conditions respectively

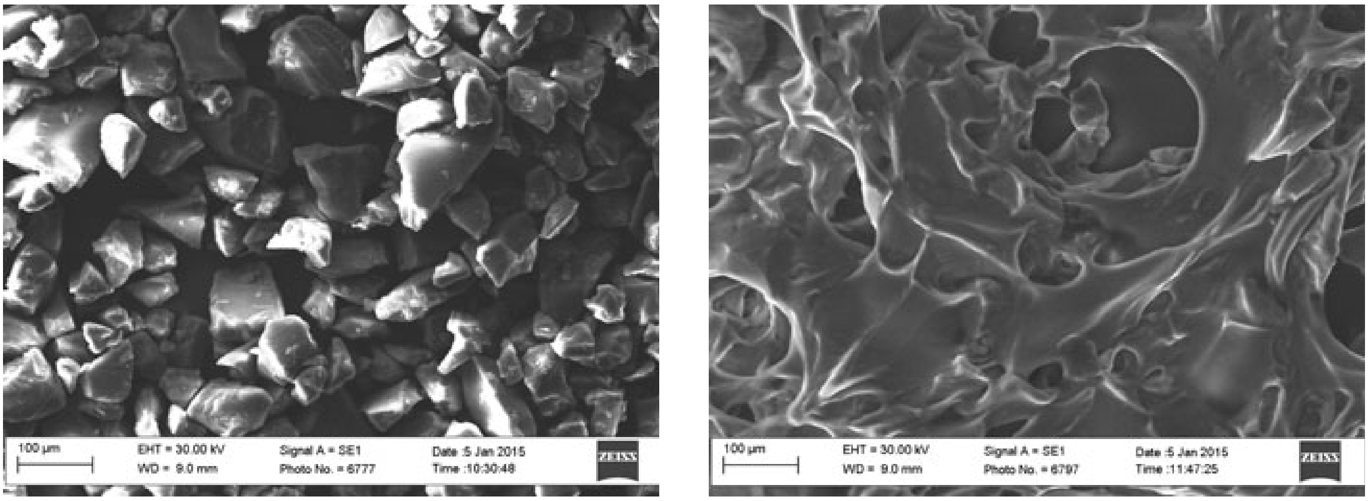

Fig. 5: The SEM micrographs of SAP Y in dry and wet conditions respectively

Application of SAP in cementitious materials

The concept of SAP as an admixture for cementitious materials is not quite new. Despite the fact that the first patents were written by DOW and Hoechst, as early as 1989 and 1996, these polymers were never introduced into the market [5]. Many studies have been carried out since then [4-9,11-14, 19-31], in order to understand the mechanisms of SAPs interactions and their effect on the properties of concrete, such as autogenous shrinkage and mechanical properties. The current paper aims to illustrate the effect of two types of SAPs on cementitious materials by considering mortars with mix proportion of 1:2 (CEM I 52.5N : fine sand) and with water-to-cement ratio (w/c) of 0.5. Reference mortars (Ref) without SAP have been used as comparison. Figures 4 and 5 show the SEM micrographs of SAPs with different water absorption capacity in dry and wet condi-

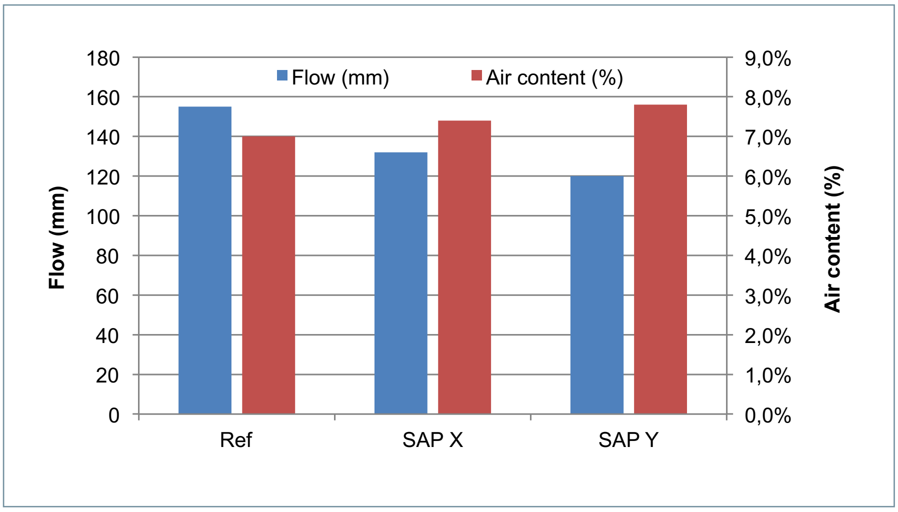

Fig. 6: Flow and air content results for mortar with and without SAPs

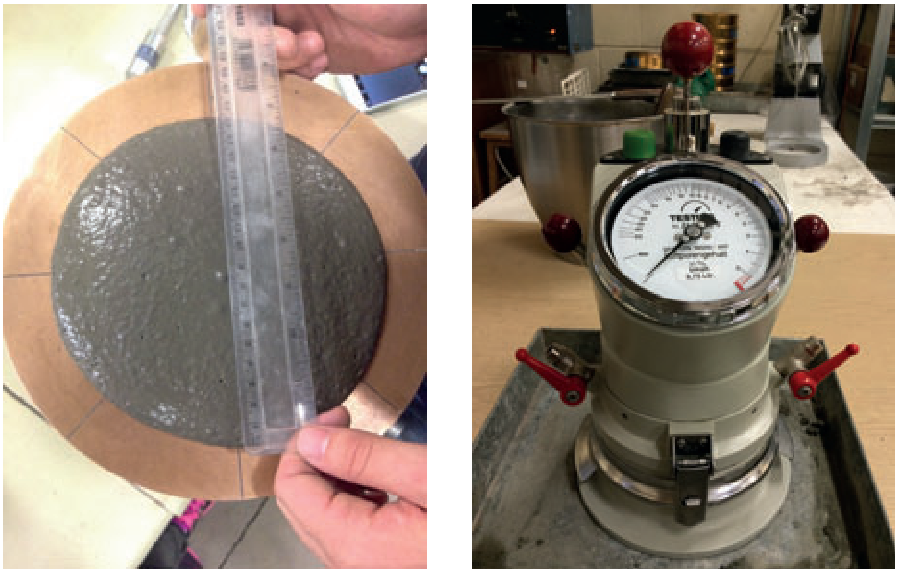

Fig.7: Flow and air content testing, respectively

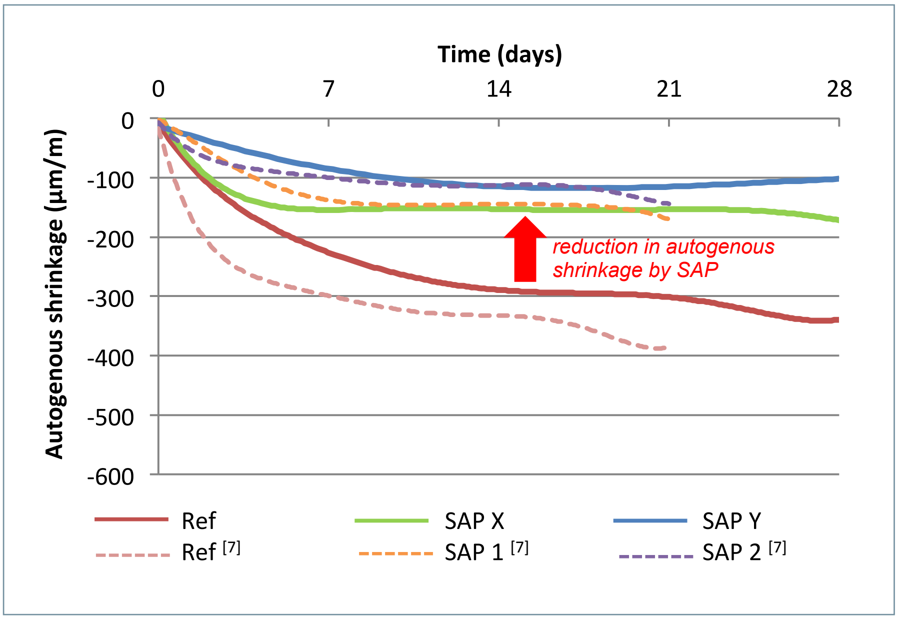

Fig. 8: Results of autogenous shrinkage testing and comparison with [7]

tions. Despite the fact that both SAPs have the same absorption capacity in demineralised water (200-250 ml/g) their absorption capacities in cement paste solution differ significantly and are respectively 25-30 g/g and 35 g/g for SAP X and SAP Y.

Autogenous shrinkage

The effect on autogenous shrinkage may be considered as the main advantage of using SAP in cementitious materials. The principle of internal curing by means of SAP relates to the provision of water-filled cavities in hardened mortars and reducing autogenous shrinkage [14]. In other words, SAP may provide water during the acceleration period of the cement hydration process, leading to decrease in self-desiccation and, hence, mitigating autogenous shrinkage. In practical terms, cement-based materials with SAP as internal curing agent may present lower cracking susceptibility, leading to more durable and better performance materials.

Several studies have been published showing the positive effect of SAP in reducing autogenous shrinkage [5-9, 11, 27]. All authors have found considerable decrease in autogenous shrinkage as a consequence of internal curing. The consistent results demonstrated clearly that internal curing through SAP is a robust approach, working independently of some variations in raw materials of concrete, production process, or measuring technique [9].

Besides the effect of water provision for internal curing, autogenous shrinkage may

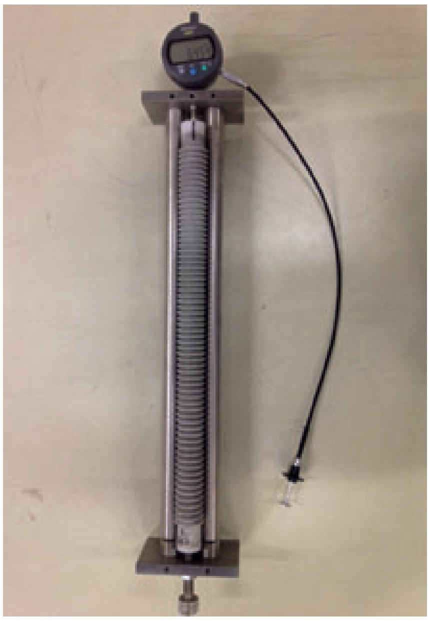

Fig. 9: Autogenous shrinkage testing by corrugated tubes method

also be influenced by more porous structure given by SAP in fresh mixtures. Usually, mixtures with SAP may present higher air content due to high absorption of water and to the swelling process when water gets into polymer.

The incorporation of air can lead to less compacted mixtures, resulting in more porous structure of matrices. Consequently, autogenous shrinkage is expected to be reduced due to the larger capillaries that lead to lower tensile stresses generated by water menisci in the capillaries. The surface tension of water, caused by the loss of water in the capillary pores, leads to increased attraction forces between pore walls, resulting in shrinkage [17].

Moreover, concrete with SAP has less "free water" to contribute to these tensile stresses. This water is absorbed by SAP resulting in drier mixes (with lower consistency). Therefore, the higher air content and the lower "free water", the tensile stresses in the capillaries are lower and concrete is less prone to deformation. Figure 6 shows mixtures with SAP present lower consistency (by flow test [15]) and higher air content (by pressure method [16]) (Figure 7).

Figure 8 shows the autogenous shrinkage results of the current study for mortars with and without SAPs and the results previously published in [7]. Autogenous shrinkage was measured by the corrugated tubes method (Figure 9) from the time of final setting until the age of 28 days [18]. In all cases SAPs notably reduced autogenous shrinkage when compared to both reference mortars.

The higher degree of hydration facilitated by CEM I, without using any extra mechanism for internal curing, leads to faster and greater self-desiccation, resulting in more considerable autogenous shrinkage. However, in the presence of SAPs, this behaviour is sharply altered showing a significant reduction. At 28 days, SAPs provided a reduction in order of 50% and 70%, respectively for samples X and Y, in comparison to the reference mortar. The similar pattern was observed for SAP1 and SAP2 samples. It illustrates the clear effect of SAP in reducing autogenous shrinkage.

The difference in SAPs performance in mitigation of autogenous shrinkage may be related to their kinetics of water absorption and desorption in cement pore solution. SAPs with slower release are more advantageous for internal curing since there is more water available for cement reaction over time and autogenous shrinkage may be mitigated. SAPs providing an intense release of absorbed pore solution during the first few hours are less efficient in reducing autogenous shrinkage because the rest of internal curing water is consumed. Therefore, the amount and duration of water release from SAP into the cementitious materials are crucial to the efficient mitigation of autogenous shrinkage [9,11].

Overall, if autogenous shrinkage is reduced by SAP, the cracking susceptibility in cement-based materials is decreased. This positive effect can lead to more durable materials and enhancement of construction sustainability by the improvement of concrete resource productivity. In general view, if concrete elements are less crack-prone and therefore less permeable, the embedded steel reinforcement will be more resistant to any corrosion processes. This more resistant material might avoid progressive deterioration of structures over their service life and, saving resources for the maintenance, repair or even replacement. Besides that, wastes generated from these repair and replacement activities would be reduced and consequently, the environmental impacts would be decreased, leading not only to more durable but also to more sustainable concrete-made buildings.

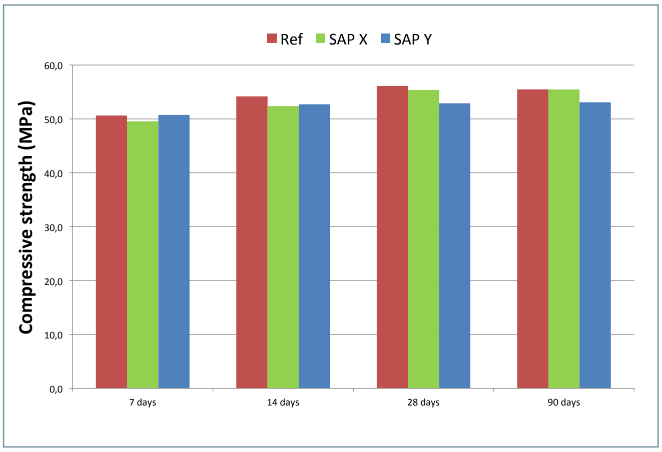

Fig. 10: Results of compressive strength

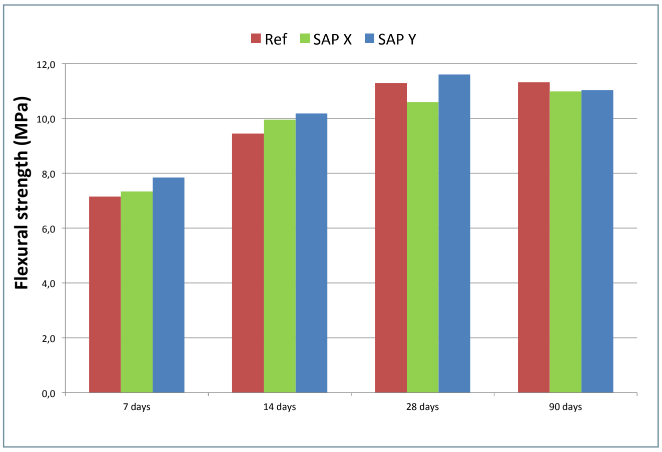

Fig. 11: Results of flexural strength

Mechanical properties

Previously published investigations show that the application of SAP may lead to some losses in compressive and flexural strengths [7, 19-23]. However, there is still no consensus on a typical performance as different polymers result in different microstructural features [8,9,11].

The decrease in mechanical properties, especially flexural strength, can be attributed to a higher pore volume in the mixes containing SAP. While giving up the internal curing water, SAP shrink and leave behind air voids, which act as weak spots in the material structure [9].

Because of this, the shape and size of the SAP particles may have a major influence on the strength values. Concrete modified by SAP with spherical and smaller particles may lead to higher strengths in comparison to a mix with irregularly shaped and larger SAP particles. Irregular pore shape left by irregular SAP particles may cause higher stress concentrations in concrete, resulting in a less resistant material. This effect is aggravated in combination with larger particles of SAP, since they will leave behind larger voids [9, 24].

The kinetics of water release in cementitious materials must also be considered. A premature release of water, i.e., before setting, into the cement-based pastes containing SAP may lead to a decrease in compressive strength. This effect can be attributed to some increase in the effective water/cement ratio and subsequently to higher porosity of concrete [11,25]. However, the pores created by SAP may be 'ink-bottle' and/or closed and consequently their effect on the overall durability may not be significant [8].

In contrast, for mixes with SAP that do not exhibit early water desorption, either no decrease or only a very moderate decrease in strength can take place. This may be explained by the release of stored water at later stages. In this case extra water may serve truly as internal curing water. The efficient mitigation of autogenous shrinkage and the enhanced degree of hydration seem to be sufficient to balance the negative effect of voids induced by SAP particles, since they have low desorption ratio [11].

To confirm this point, some studies [8, 26-31] have shown that there is a minimal loss of compressive strength or there may even be a small strength gain. It is generally accepted that SAP increase a degree of hydration and can prevent concrete from self-desiccation. Consequently a denser paste phase is obtained and propagation of microcracks is prevented.

Figures 10 and 11 respectively show the results of compressive and flexural strength testing of reference mortar and mortars with SAP X and Y, at 7, 14, 28 and 90 days [32]. It seems that SAPs do not have a significant effect on mechanical properties, especially for advanced ages (90 days) leading to the conclusion that both SAP X and Y may be used as internal curing agents.

However, the effect of SAP type on development of microstructure of the cement-based matrix is yet to be thoroughly investigated in order to develop a substantiated mechanistic explanation for the macroscopic finding [11].

In summary, mechanical properties are much related to the type of SAP, which can lead to either decrease or a small gain in strength. However, those differences do not seem to be sufficiently significant to exclude SAP use in cementitious materials. The necessity for more studies of SAPs absorption and desorption mechanisms in hardened cement-based matrices are very evident.

Final considerations and outlook

Superabsorbent polymers (SAP) can be considered as a new admixture for cementitious materials in order to control internal curing in fresh and hardened state. Their application in concrete and mortars can positively affect properties, such as, autogenous shrinkage and flexural and compressive strength.

Autogenous shrinkage is clearly reduced by SAPs, making this outcome the main agreed advantage for using SAP. Since autogenous shrinkage is reduced, the cracking susceptibility is decreased, leading to production of more durable and sustainable cementitious materials.
Mechanical properties can be easily affected by the type of SAP, its particle sizes, shapes, and absorption and desorption features. The capacity and kinetics of SAP sorption, as well as, the characteristics and compositions of the cementitious materials where SAP is added, have major influence on the compressive and flexural strength.
Therefore, SAP show themselves to be a potential and promising novel material to be used as internal curing agents for concrete and mortars in order to control self-desiccation processes.

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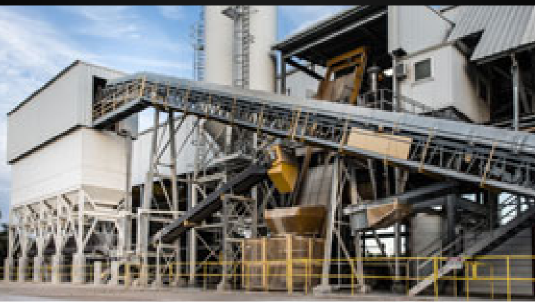

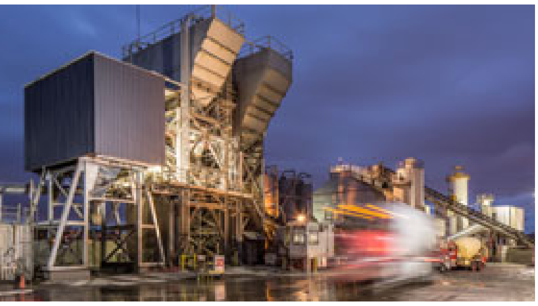

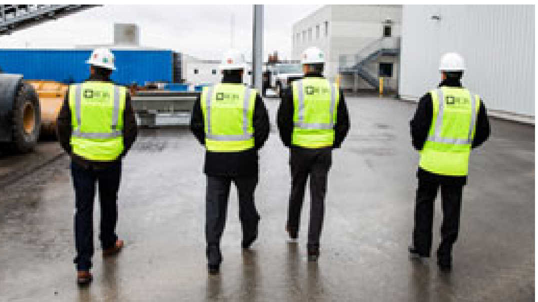

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